

Liquid-liquid Extraction of Au(I) by Amberlite LA2 and its Application to a Polymer- Immobilized Liquid Membrane System

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Abstract

The liquid-liquid extraction of Au(I) by Amberlite LA2 (secondary amine) in kerosene from cyanide media has been investigated. The analysis of metal distribution data suggested the formation of $R_2NH_2^+Au(CN)_2^-$ species in the organic phase with formation constant $\log K_{\text{ext}} = 6.5 \pm 0.03$, whereas the use of mixtures of the amine with a solvation extractant (e.g. a phosphine oxide) shifted the gold- $pH_{1/2}$ extraction towards more alkaline values. The results obtained on Au(I) distribution have been implemented in a polymer-immobilized liquid membrane system, using NaOH solutions (e.g. 0.01 mol/L) to strip the metal from the organic phase.

Keywords – Liquid-liquid extraction.

Membrane transport. Gold (I). Amberlite LA2

Introduction

Gold is usually recovered from various resources by cyanidation. The corresponding metal-rich solutions need to be concentrated to produce a higher grade solution from which gold can be most efficiently obtained by the corresponding recovery methods. The concentration of the gold-bearing solutions is normally carried out by carbon adsorption or ion exchange [1]. Liquid-liquid extraction had no known practical application in this field, though in the latter years there has been a renewed interest in the application of this technique to the recovery of this precious metal from such alkaline solutions using various extractants [2-5]. These extraction systems can also be implemented in solid supported liquid membranes where the performance of the separation operation is enhanced by a combination of the extraction and stripping processes in one step. The application of this technology in the treatment of dilute gold (I) cyanide-bearing solutions is also described in the literature [6,7].

The present investigation was undertaken to characterise quantitatively the extraction reactions between aqueous Au(I) and Amberlite LA2 extractant in kerosene. Furthermore, a liquid membrane system has been designed using the extraction process mentioned above, and parameters affecting the liquid membrane have been studied.

Experimental

The secondary amine Amberlite LA2 (Fluka) was used as received, the purity was greater than 95% (experimentally determined by titration of the reagent with standard HCl solutions). The organic phase was prepared by diluting a measured volume of the amine with the as-received corresponding diluent: kerosene (20% aromatics), cumene (AR grade), toluene (AR grade), decane (AR grade) or xylene (AR grade). Kerosene is a product of Campsa (Spain). Cyanex 921 (99% tri-n-octylphosphine oxide, CYTEC) and TBP (tri-n-butylphosphate, AR grade) extractants were also used without further purification. Stock solutions of gold were prepared by dissolving $KAu(CN)_2$ (AR grade) in distilled water. All other chemicals were of AR grade.

Extraction experiments were carried out in thermostatically controlled separatory funnels by shaking (700 min^{-1}) together equal volumes of the corresponding aqueous and organic phases at 20°C for the time required. The concentration of gold in the aqueous solutions was measured by AAS using a Perkin Elmer 1100B spectrophotometer. The concentration of the metal in the organic solutions was calculated from the mass balance. From these data, the distribution coefficient D_{Au} was calculated as the ratio

$$D_{\text{Au}} = \frac{[Au]_{\text{org}}}{[Au]_{\text{aq}}} \quad (1)$$

where $[Au]_{org}$ and $[Au]_{aq}$ are the total gold concentration in the organic and aqueous phases, respectively. IR spectra were obtained in a Unicam SP3-200S double beam spectrophotometer in order to investigate probable change in the coordination of the $Au(CN)_2^-$ complex.

Permeation experiments, at the temperature of 20°C, were carried out with a two compartment permeation cell which consisted of a source phase chamber (200 ml) separated from a receiving phase chamber (200 ml) by a liquid membrane having an effective membrane area of 11.3 cm². The support for the liquid membrane was a polyvinylidenedifluoride film (Millipore Durapore GVHP) with a thickness of 124 µm, porosity 75% and average pore size 0.22 µm. The liquid membrane was prepared by impregnating the laminar microporous film with the corresponding Amberlite LA2 solution for 24 hours, then leaving it to drip for ten seconds before being placed in the permeation cell. In each experiment, stirring rate in both the source and receiving solutions was kept constant at 1400 rpm. Membrane permeabilities were determined by monitoring Au(I) concentrations by AAS, using the same apparatus as above, in the source phase as a function of time. Permeability coefficient, P_{Au} , was calculated from

$$\ln \frac{[Au(I)]_t}{[Au(I)]_0} = \frac{A}{V} P_{Au} t \quad (2)$$

where $[Au(I)]_t$ and $[Au(I)]_0$ are the metal concentration in the source phase at an elapsed time and time zero, respectively, A is the effective membrane area, V is the volume of the source solution and t is the time.

The same procedure, as described above, was used to study either the extraction or the permeation of the different metal-cyano complexes investigated in the present work.

Results and discussion

Extraction

Preliminary experiments were carried out in order to determine the time needed to achieve equilibrium. From the results obtained, at 0.1 mmol/l Au(I), pH_{eq} 5.0±0.02 and 0.046 M Amberlite LA2 in kerosene, equilibrium is observed to be reached after 5 min of mixing. Nevertheless, the contact time was fixed at 15 min.

The metal distribution ratio, D_{Au} , at various equilibrium pH values (pH_{eq} 5-6.5) was determined for 0.23 M Amberlite LA2 in kerosene at Au(I) concentrations ranging 0.05-0.25

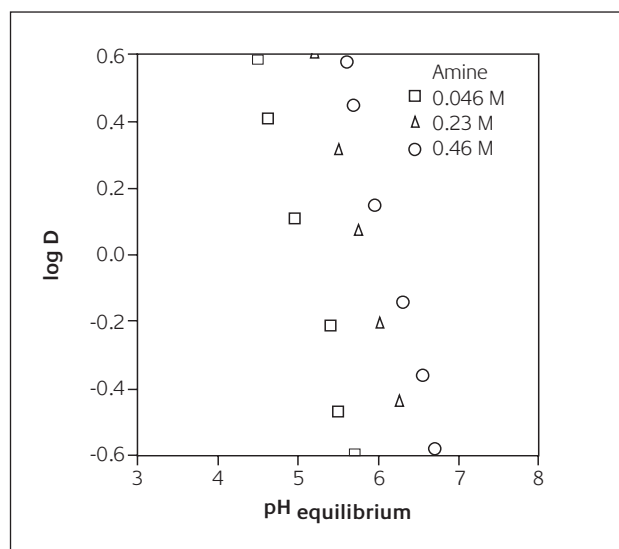
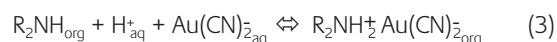


Figure 1

Gold (I) cyanide extraction by different amine concentrations in kerosene

mmol/l. The results show that D_{Au} (e.g. 5 at pH_{eq} 5 or 0.2 at pH_{eq} 6.5) does not depend on the gold concentration, this behaviour indicates that no polynuclear complexes are formed in the organic phase.

The influence of the variation in the concentration of the extractant on the distribution of gold was studied using aqueous phases of 0.1 mmol/l gold and organic phases of the amine in kerosene. Figure 1 shows that gold extraction increases as the amine concentration is increased, thus as the amine concentration is increased better gold loading in the organic phase is obtained at higher pH values. This behaviour is due to the mass action effect, shifting the metal extraction equilibrium to the right



The effect of the diluent of the organic phase on metal extraction was also studied. In this case, organic phases of the amine (0.046 M in kerosene or cumene) were contacted with aqueous phases of 0.05 mmol/l gold (I) at different pH values. Results obtained showed that the $pH_{1/2}$ values (see Table 1 for the definition of $pH_{1/2}$) for gold extraction are 5.1 and 5.5 using kerosene or cumene, respectively, as diluents of the organic phase.

Table 1

$pH_{1/2}$ values for the extraction of cyano complexes with the amine Amberlite LA2 and the amine/Cyanex 921 mixture

Anion	Structure	^a $pH_{1/2}$	^b $pH_{1/2}$
$Au(CN)_2^-$	Linear	5.1	7.8
$Ni(CN)_4^{2-}$	Square planar	5.3	5.7
$Fe(CN)_6^{3-}$	Octahedral	4.6	4.7

$pH_{1/2}$ is defined as the equilibrium pH value in which $\log D_{Au} = 0$.

^aOrganic phase: 0.046 M Amberlite LA2. ^bOrganic phase: 0.046 M Amberlite LA2 and 0.052 M Cyanex 921.

The influence of a background electrolyte, such as Na₂SO₄, was investigated by contacting gold (I) cyanide solutions, 0.1 mmol/l gold, with and without 0.5 M or 1 M Na₂SO₄, and 0.12 M Amberlite LA2 in kerosene. There was little or no effect on gold extraction due to the inert electrolyte, so it was concluded that ionic strength was not significant in determining the extent of gold extraction with this particular amine.

An infrared spectrum of an amine-gold (I) cyanide solution in kerosene, 0.12 M amine and 17.9 mmol/l gold, pathlength 0.1 mm and KBr windows, showed an absorption peak at near 2150 cm⁻¹ that can be assigned to the CN stretching frequency for the Au(CN)₂⁻ anion [8]. There is not appreciable change in the CN stretching frequency compared to that reported for this anion so it can be deduced that there is no specific interaction of the amine with the gold (I) complex; the Au(CN)₂⁻ anion seems to be inert to increased coordination [9].

When a potential extraction system is considered for the extraction of a given metal, it is important to take into account certain selectivity considerations in the extraction of other metals that could be present in the aqueous solution which could interfere with the main extraction system. This should be the case of gold-cyanide processing, in which the presence of other metal-cyano complexes is often found in the aqueous solution. Thus, the possibility of separation of gold from those complexes was also studied. Extraction experiments carried out at 20°C and at organic:aqueous phase ratio of 1:1, using an organic phase containing 0.046 mmol/l of the amine in kerosene and aqueous phases containing 1.5 mmol/l of each metal (Au(I), Ni(II) and Fe(III)) show (Table 1) that these metal-cyanide complexes were all extracted under acidic or slightly acidic conditions and the selective extraction of gold is not possible under these conditions.

Further investigations were, thus, done to improve the separation of gold from other metals accompanying the precious metal in the cyanide solution. The use of mixtures of the amine with solvation reagents had been study, since these mixtures seem to be attractive for the extraction of gold (I) from alkaline solutions [2,10]. This study was carried out shaking equal volumes of organic phases of amine Amberlite LA2 (0.12 M) plus Cyanex 921 (0.13 M) or TBP (0.18 M) in kerosene and aqueous phases of gold (I) cyanide, 0.1 mmol/l gold. The results are shown in Table 2 in which the values of the pH_{1/2} for gold extraction are shown. As can be seen from this table, adding the above mentioned solvation

Table 2

pH_{1/2} values for the extraction of gold using the amine Amberlite LA2 and mixtures of the amine with TBP or Cyanex 921

Extractant	pH _{1/2}
Amberlite LA2	5.5
Amberlite LA2 and TBP	7.0
Amberlite LA2 and Cyanex 921	9.0

Table 3

Influence of increasing amine Amberlite LA2/Cyanex 921 concentrations on gold (I) cyanide extraction

Amine/Cyanex 921	pH _{1/2}
0.046 M/0.052 M	7.8
0.12 M/0.13 M	9.0
0.23 M/0.26 M	9.9

Aqueous phase: 0.1 mmol/l gold

extractants to the organic phase shifts the pH_{1/2} to higher pH values, allowing gold extraction from neutral or even alkaline solutions (as obtained from cyanide-leaching operations). From these results, also can be deduced that this effect increases in the order Cyanex 921 (phosphine oxide)>TBP (phosphoric ester), that is, as the electron donor properties of the extractant increase.

Since with the amine/Cyanex 921 mixture the best extraction results were obtained, further studies had been carried out employing this mixture. In Table 3 is shown the variation in the gold extraction pH_{1/2} value when various concentrations of the reagents mixture is used to extract gold. The results showed that increasing the extractant mixture concentration, gold is allowed to be extracted at more alkaline pH values. If this mixture amine-Cyanex 921 is employed, the extraction sequence shown in the extraction of metal-cyano complexes (Table 1) will change; in this same table is shown the pH_{1/2} for metal extraction obtained for a series of experiments carried out with organic phases of the amine (0.046 M) and Cyanex 921 (0.052 M) in kerosene and aqueous solutions which contained 1.5 mmol/l of the corresponding metal. From this table it can be seen that the addition of Cyanex 921 to the amine solution allowed the selective extraction of gold (I) cyanide from aqueous solutions (difference in the pH_{1/2} value greater than one unit), and in general the extractability order of the metal-cyano complexes by the amine Amberlite LA2-Cyanex 921 extraction system follows the series: M(CN)₆³⁻<M(CN)₄²⁻<M(CN)₂⁻. Those metals which form complexes of lower coordination number will be extracted favourably over those with higher coordination number; this order is the same as obtained for cyanide complexes with other amine/Lewis Bases or other reagents [11-13].

Experimental data were treated numerically using the program LETAGROP-DISTR [14], in order to gain knowledge about the stoichiometry of the species involved in the extraction of gold (I) by the amine and the amine-Cyanex 921 mixture and to obtain the values of the equilibrium constants. In this program, the error square sum U defined as

$$U = \sum (\log D_{\text{cal}} - \log D_{\text{exp}})^2 \quad (4)$$

was used in the minimisation process. D_{exp} represents the experimental distribution coefficient and D_{cal} is the value calculated by the program for the model tested after solving

Table 4

Species and extraction constants for gold extraction by the amine Amberlite LA2 and the amine Amberlite LA2/Cyanex 921 mixture

System	Species	Log K_{ext}	$\sigma(\log K_{\text{ext}})$	U
Amine	$R_2NH_2^+Au(CN)_2^-$	6.5 ± 0.03	0.01	0.04
Amine/Cyanex 921	$R_2NH_2^+Au(CN)_2-L$	9.7 ± 0.1	0.05	0.01
	$R_2NH_2^+Au(CN)_2-L_2$	11.0 ± 0.2		

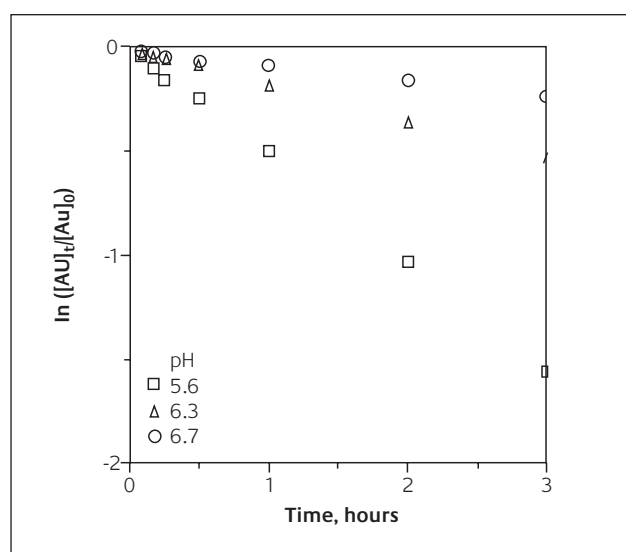
L = Cyanex 921

the mass balance equations of the components of the system. Thus, the best model is the one which gives the lowest value of U. The calculations were carried out taking a set of species and extraction constants as the starting input and considering the influence of the minimised function when partially varying or adding new species to the model. According to the results obtained (Table 4), the numerical program fits the existence of one and two species in the organic phase for the extraction of gold (I) by the amine and the amine-Cyanex 921 mixture, respectively.

Membrane transport

The extraction system of gold (I)-Amberlite LA2 has been implemented in a polymer-immobilized liquid membrane, where the transport of gold species across the liquid membrane depends not only on the equilibrium distribution ratios but also on the kinetics of the extraction and stripping process. However, previous tests had shown that in the present system gold is easily strippable from loaded organic solutions using 0.01 M sodium hydroxide solution, thus this variable was not investigated in the present study.

Firstly, the effect of carrier diluent on the permeability of gold (I) was studied. The membrane diluent chosen as a water-resistant barrier in any liquid membrane process exerts a major influence on membrane performance [15]. It was concluded that the polarity of the diluent is the most decisive factor in determining effectiveness as a membrane medium; on the

**Figure 2**

Influence of pH on gold transport

Table 5

Influence of membrane diluent on gold transport

Diluent	P (cm/s)
Toluene	$4.4 \cdot 10^{-4}$
Cumene	$7.0 \cdot 10^{-4}$
Decane	$8.0 \cdot 10^{-4}$
Kerosene	$6.6 \cdot 10^{-4}$
Xylene	$2.3 \cdot 10^{-3}$

Source phase: 0.025 mmol/L gold at pH 6.0 ± 0.02 . Membrane phase: 0.46 M Amberlite LA2

Table 6

Influence of the initial metal concentration on gold transport

Au (mmol/l)	P (cm/s)
0.025	$7.5 \cdot 10^{-3}$
0.05	$2.3 \cdot 10^{-3}$
0.1	$7.5 \cdot 10^{-4}$

Source phase: gold solutions at pH 5.0 ± 0.02

other hand, the membrane stability versus rapid transport is the major choice to be made in selecting a membrane diluent [16]. The diluent employed as a membrane should retain the carrier to the maximum extent and yet at the same time retain a relatively high concentration of water to aid in the transfer of hydrated species without loss of carrier to the aqueous solution. In the present study, gold permeation is dependent on the diluent used to dissolve Amberlite LA2 reagent; excellent gold (I) permeation was achieved using xylene, thus, this diluent was chosen for further gold permeation studies. The transport of gold using various diluents is presented in Table 5.

The single ion transport through the liquid membrane of 0.025 mmol/l Au(I) from an aqueous source phase adjusted to varying pH (5.6 to 6.7) values was studied using 0.23 M amine Amberlite LA2 in xylene as membrane phase. Figure 2 shows that as the pH value of the source phase increases, the permeability of gold decreases.

The influence of the initial Au(I) concentration in the source side on transport across the liquid membrane containing 0.46 M Amberlite LA2 is shown in Table 6. It can be seen that gold transport through the polymer-immobilized liquid membrane is increased as the initial gold concentration decreases.

The influence of the membrane composition was also

Table 7

Gold permeability vs. carrier concentration

^a Amine	^a P (cm/s)	^b Amine/Cyanex 921	^b P (cm/s)
0.046 M	3.8·10 ⁻⁴	0.046 M/0.052M	4.1·10 ⁻⁴
0.23 M	1.3·10 ⁻⁴	0.12 M/0.13 M	1.0·10 ⁻³
0.46 M	1.8·10 ⁻³	0.46 M/0.52 M	2.4·10 ⁻³

^aSource phase: 0.025 mmol/l gold at pH 6.2±0.02. ^bSource phase: 0.025 mmol/l gold at pH 10.0±0.02**Table 8**

Metal transport for various metal-cyano complexes

Anion	^a P (cm/s)	^b P (cm/s)
Au(CN) ₂ ⁻	1.1·10 ⁻³	2.4·10 ⁻³
Ni(CN) ₄ ²⁻	3.9·10 ⁻⁴	no metal transport
Fe(CN) ₆ ³⁻	8.2·10 ⁻⁷	no metal transport

^aSource phase: 0.025 mmol/l metal at pH 6.6±0.02.

Membrane phase: 0.46 M Amberlite LA2

^bSource phase : 0.025 mmol/l metal at pH 10.0±0.02. Membrane phase: 0.46 M Amberlite LA2 and 0.52 M Cyanex 921

studied. Table 7 shows permeability values for the transport of gold through a liquid membrane impregnated with solution 0.046-0.46 M Amberlite LA2 in xylene. As it should be expected, the permeability value increases with Amberlite LA2 concentration, this may be due to an increase in extractability into the membrane.

The behaviour of Au(I) together with other metal-cyano complexes was examined in order to study the selectivity of Amberlite LA2 polymer-immobilized liquid membrane. The results of metal permeability are shown in Table 8, and partially selective permeation of Au(I) over nickel and iron is observed.

The results obtained show that, similarly to liquid-liquid extraction, the use of a supported liquid membrane impregnated with the amine Amberlite LA2 does not allow the complete separation of the Au(CN)₂⁻ complex from other metal-cyano complexes; moreover, the gold-complex is only effectively transported at neutral or slightly acidic pH values. In order to improve the performance of the membrane system, mixtures of the amine with solvation reagents were used as carriers for gold transport, and as in the case of liquid-liquid extraction investigation, Cyanex 921 and TBP were used in this study. The results concerning transport of gold (I) from the source phase containing 0.025 mmol/l gold at pH 9.2 and receiving phase of 0.01 M NaOH were obtained using organic solutions of the amine (0.46 M) and the solvation extractants (0.52 M Cyanex 921 or 0.72 M TBP) in xylene. Gold (I) permeability increases in the order Amberlite LA2-Cyanex 921 (P= 6.4·10⁻³ cm/s)>Amberlite LA2-TBP (P=9.8·10⁻⁵ cm/s)>Amberlite LA2 (P= 8.2·10⁻⁵ cm/s), which is similar to the gold extraction order obtained for these systems in liquid-liquid extraction studies.

The effect of different amine-Cyanex 921 concentration on permeability was investigated in the range 0.046-0.46 M (Amberlite LA2) and 0.052-0.52 M (Cyanex 921), with the source and stripping phases composition kept constant at

0.025 mmol/l gold at pH 10.0 and 0.01 M NaOH, respectively. As can be seen from Table 7, the permeability of gold increases with carriers mixture concentrations, and similarly to the gold transport by the amine alone, diffusion of the complex across the liquid membrane seems to be the rate determining step [17].

The selectivity of the system Amberlite LA2-Cyanex 921 was also studied against the presence of other metal-cyano complexes. For these investigations, transport experiments were carried out using a membrane phase of 0.46 M amine and 0.52 M Cyanex 921 in xylene, receiving phases of 0.01 M NaOH and sources phases which contained various metallic ions (Table 8). Results obtained, shown in this same table, indicated that the aurocyanide complex is transported preferably to other metal-cyano complexes, and at alkaline pH values. It is also observed, than the transport order obtained for these cyano complexes is the same as that obtained in liquid-liquid extraction.

The authors' thanks to Mr. Bascones and Mr. López for technical assistance. Also to the CSIC (Spain) for support.

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